[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

Reactions of Vanillin and its Derived Compounds. I. The Reaction of Vanillin with Silver Oxide[1]

BY IRWIN A. PEARL

Although vanillin has been in large scale commercial production for years, its derived acid, vanillic acid, has remained more or less a laboratory curiosity because of the lack of a satisfactory process for the direct transformation of one to the other. Vanillic acid has been prepared directly from vanillin by several different methods. Tiemann[2] obtained traces of vanillic acid by subjecting vanillin to the action of moist air for a long period of time and Ciamician and Silber[3] obtained small yields of vanillic acid by exposing vanillin to sunlight in the presence of nitrobenzene. Robbins and Lathrop[4] isolated small amounts of the acid as an intermediate product in the reactions taking place when certain soil bacteria act upon vanillin, and Dorland and Hibbert[5] obtained 21% of vanillic acid by oxidation of small amounts of vanillin with ozone in ethyl acetate. Lock[6] and Sabalitschka and Tietz,[7] on fusion of vanillin with potassium hydroxide, obtained mixtures of vanillic acid and protocatechuic acid which could be separated only by a laborious fractionation. Two indirect methods for the preparation of vanillic acid from vanillin have been reported. Böeseken and Greup[8] acetylated vanillin, oxidized the resulting acetylvanillin with peracetic acid, and hydrolyzed the acetylvanillic acid to vanillic acid in a low over-all yield. Raiford and Potter[9] obtained good yields by alkaline hydrolysis of acetylvanillonitrile which, in turn, was prepared by treatment of vanillin oxime with acetic anhydride.

In a search for a simple process for converting vanillin directly into vanillic acid, it was found that silver oxide and excess alkali in aqueous solution effected this transformation.[10] In the first experiment, based on classical oxidations of aldehydes by means of silver oxide, in which one mole of silver oxide was employed for one mole of aldehyde, complete reduction of the silver oxide took place only after long boiling, and a low yield of crude vanillic acid was obtained, together with considerable resinous material. The use of one-half mole of silver oxide and excess alkali with one mole of vanillin gave a substantially quantitative transformation of vanillin to pure vanillic acid. This unexpected discovery proved that silver oxide alone did not accomplish all of the oxidation and that one of the other two substances present in the reaction mixture, namely, oxygen of the air and sodium hydroxide, must have acted as an oxidizing agent. Inasmuch as vanillin is stable when boiled with alkali in the presence of air,[11–14] because this new oxidation reaction also took place in an inert atmosphere, and because hydrogen was liberated in this reaction, it seemed probable that a Cannizzaro reaction[15] catalyzed by silver oxide (or the metallic silver formed during the reaction) might have taken place according to the following scheme, which accounts for all the observed facts.

$$\mathrm{2RCHO + NaOH \xrightarrow{NaOH} RCH_2OH + RCOONa} \qquad (1)$$

$$\mathrm{RCH_2OH + Ag_2O + NaOH \longrightarrow RCOONa + 2Ag + H_2 + H_2O} \qquad (2)$$

$$\mathrm{2RCHO + Ag_2O + 2NaOH \xrightarrow{NaOH} 2RCOONa + 2Ag + H_2 + H_2O} \qquad (3)$$

That a Cannizzaro reaction actually occurs was confirmed by a series of experiments employing less than one-half mole of silver oxide in which vanillyl alcohol (in the form of its bimolecular condensation product) was recovered in the calculated amount, depending upon the amount of silver oxide used. Thus, reaction of 1.0 mole of vanillin with 0.25 mole of silver oxide and 4.0 moles of sodium hydroxide yielded 0.26 mole of the bimolecular condensation product of vanillyl alcohol and 0.71 mole of vanillic acid. Experiments employing 0.10 mole and 0.05 mole of silver oxide gave the expected results, but the use of 0.01 mole of silver oxide did not catalyze the Cannizzaro reaction and resulted in the recovery of most of the vanillin except for the amount oxidized by the silver oxide.

Equation (2) was partially confirmed by an experiment in which a suspension of silver oxide in alkaline solution was treated with one mole of vanillyl alcohol. A 93% yield of vanillic acid was obtained. Hydrogen was indicated by gas bubbles, but no quantitative estimation could be made because most of the hydrogen was adsorbed on the fluffy silver metal.

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(2) Tiemann, *Ber.*, **8**, 1123 (1875).

(3) Ciamician and Silber, *ibid.*, **38**, 3821 (1905).

(4) Robbins and Lathrop, *Soil Sci.*, **7**, 475 (1919).

(5) Dorland and Hibbert, *Can. J. Research*, **18B**, 33 (1940).

(6) Lock, *Ber.*, **62**, 1187 (1929).

(7) Sabalitschka and Tietz, *Arch. Pharm.*, **269**, 545 (1931).

(8) Böeseken and Greup, *Rec. trav. chim.*, **58**, 528 (1939).

(9) Raiford and Potter, THIS JOURNAL, **55**, 1682 (1933).

(10) For the preliminary announcement of this reaction see Pearl, THIS JOURNAL, **67**, 1628 (1945).

(11) Raikow and Raschtanow, *Oesterr. Chem. Ztg.*, **5**, 169 (1902).

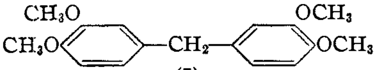
(12) Lock, *Ber.*, **62**, 1181 (1929).

(13) Tomlinson and Hibbert, THIS JOURNAL, **58**, 348 (1936).

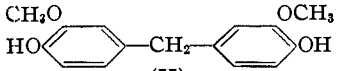
(14) Geissman, Chapter 2 in Adams, "Organic Reactions," Vol. II, John Wiley and Sons, New York, N. Y., 1944, p. 104–107.

(15) The catalyzed Cannizzaro reaction of vanillin will be the subject of a subsequent paper in this series.

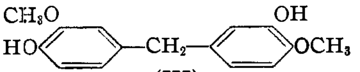
It is interesting to note that vanillyl alcohol as such was never isolated from the reaction mixtures. However, carbon dioxide acidification of the alkaline solution always yielded a light tan semisolid material which was easily recrystallized from water or ligroin to silky white needles melting at 108–109°. Sulfur dioxide acidification of the original alkaline reaction mixture yielded a light tan resinous material smelling of formaldehyde. Recrystallization of this resinous product also gave needles melting at 108–109°, identical with those above. Analysis of the pure compound and of its dibenzoate indicated it to be a dihydroxydimethoxydiphenylmethane. The dimethyl ether, prepared by methylation with dimethyl sulfate and alkali, was identical with Robinson's[16] 3,4,3′,4′-tetramethoxydiphenylmethane (I) prepared by reducing the corresponding benzophone.



(I)



(II)



(III)

Therefore, the original compound must have been either 4,4′-dihydroxy-3,3′-dimethoxydiphenylmethane (II) or 4,3′-dihydroxy-3,4′-dimethoxydiphenylmethane (III). Formula (II) assumes that formaldehyde and water split off between two alcohol groups and formula (III) assumes that condensation took place meta to the hydroxyl group with subsequent splitting off of formaldehyde. Because phenolic hydroxyl groups are strong ortho- and para-directing groups and because (III) could be formed only by meta-substitution, together with the fact that formula (II) type condensations are well known in "Bakelite" type resin reactions, the compound must be 4,4′-dihydroxy-3,3′-dimethoxydiphenylmethane (II).

To prove that vanillyl alcohol must have been formed as the product of the catalyzed Cannizzaro reaction of vanillin and that the vanillyl alcohol thus formed underwent condensation to produce (II), vanillyl alcohol, both alone and with vanillic acid, was treated with aqueous alkali under conditions simulating the vanillin reactions. The alkaline reaction mixtures on partial acidification with carbon dioxide (while still strongly alkaline) deposited semisolid masses which gave white crystals of 4,4′-dihydroxy-3,3′-dimethoxydiphenylmethane upon recrystallization from water or ligroin. This indicates that the vanillyl alcohol formed as the primary product of the Cannizzaro reaction actually reacts in the alkaline solution to form the bimolecular condensation product (II). This type of condensation usually takes place in acid solution.[17,18]

Hydrogen was identified in the reaction products of the oxidation reaction employing one-half mole of silver oxide by performing the reaction in a closed system under nitrogen. The evolved gas was carried in succession through a sulfuric acid wash bottle, a drying tube filled with Anhydrone, a combustion tube filled with glowing cupric oxide wire, a weighing tube filled with Anhydrone, and an Anhydrone drying tube. The amount of hydrogen recovered, calculated from the water obtained on oxidation over glowing copper oxide, amounted to 5–10% of the theoretical according to equation (3). However, most of the hydrogen liberated in the reaction was adsorbed on the porous metallic silver, resulting in a very fluffy silver metal having an apparent specific gravity of 0.7–0.9. Furthermore, long boiling of this fluffy silver in water resulted in the liberation of more hydrogen.

Dinelli,[19] because of his work on several easily oxidizable aldehydes, reported that cupric oxide prepared in the presence of silver oxide could be used in place of silver oxide for oxidizing aldehydes to acids, although cupric oxide alone had no effect upon aldehydes. Dinelli's conditions were duplicated with vanillin, but vanillic acid was obtained only in an amount corresponding to the silver oxide present.

The fluffy silver precipitate formed in the vanillin reaction can be oxidized very readily by means of potassium permanganate and be reused for further oxidations without resorting to the involved process of conversion to silver nitrate and reprecipitation with alkali.

Experimental

All melting points given are uncorrected.

Reaction of Vanillin with Alkali and One Mole Silver Oxide.—A solution of 68 g. (0.4 mole) of silver nitrate in 350 cc. of water was treated with a solution of 16 g. (0.4 mole) of sodium hydroxide in 150 cc. of water. The precipitated silver oxide was stirred for a short time, filtered, and washed free of nitrates with water. The wet, freshly precipitated silver oxide was transferred to a 1-liter reaction flask, covered with 400 cc. of water and, with stirring, treated in succession with 40 g. (1.0 mole) of sodium hydroxide and 30.4 g. (0.2 mole) of vanillin. The mixture was then heated to boiling under reflux for two hours. Much of the silver oxide appeared to be reduced immediately, but the rest did not disappear until approximately one hour had passed. The precipitate, which consisted of pure silver granules, was filtered and washed with water. The yield of dried silver was 43.2 g., *i. e.*, quantitative. The combined filtrate and washings were acidified with sulfur dioxide, giving a yellow precipitate. The mixture was extracted with ether, but considerable precipitate would not dissolve. The evaporated ether and the undissolved solid were extracted with 8% sodium bicarbonate solution. Acidification of the bicarbonate extract, followed by recrystallization of the yellow precipitate (24 g.) from hot water containing decolorizing carbon, yielded 16.8 g. (50%) of semi-pure vanillic acid as white needles melting at 206–208°. The nature of the yellow

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[16] Robinson, *J. Chem. Soc.*, **107**, 273 (1915).

[17] Baekeland and Bender, *Ind. Eng. Chem.*, **17**, 225 (1925).

[18] Megson and Drummond, *J. Soc. Chem. Ind.*, **49**, 251 (1930).

[19] Dinelli, *Ann. Chim. Applicata*, **29**, 448 (1931).

resinous material insoluble in ether and bicarbonate was not determined.

Reaction of Vanillin with Alkali and One-Half Mole Silver Oxide.—Silver oxide (0.1 mole), prepared as above from 34 g. (0.2 mole) of silver nitrate and sodium hydroxide, was placed in a beaker and covered with 400 cc. of water. With vigorous stirring 40 g. (1.0 mole) of solid sodium hydroxide was added, bringing the temperature of the mixture to 55°. With continued stirring 30.4 g. (0.2 mole) of vanillin was added at one time. In a few moments reaction set in, the silver oxide was reduced to fluffy metallic silver, and the temperature of the reaction mixture reached 85°. No outside heat was applied. The mixture was filtered, and the silver precipitate was well washed with water and dried to give 21.5 g. (100%) of fluffy silver having an apparent specific gravity of 0.85. The combined filtrate and washings were acidified. The white needles which separated were filtered, washed with water, and dried to give 31 g. (92.3%) of pure vanillic acid melting at 210–211°. The melting point of a mixture with authentic vanillic acid[9] was not depressed. Ether extraction of the sulfur dioxide-saturated filtrate yielded an additional 1.5 g. (4.5%) of semi-pure vanillic acid melting at 206–208°.

It was found that 50–55° was the critical temperature for this reaction. If the reactants were mixed cold, the mixture required added heat to bring the temperature above 50° to initiate the reaction. Mixing of the reactants at temperatures much higher than 55° resulted in uncontrollable reaction mixtures.

Reuse of Fluffy Silver.—The wet fluffy metallic silver (21.5 g., 0.2 atom) from the last experiment was gradually added to a well stirred solution of 13.4 g. (0.083 mole) of potassium permanganate in 100 cc. of water. After several minutes the solution turned deep green in color. The red color was restored with a little more permanganate, and the mixture was filtered. After washing free of permanganate, the silver oxide was transferred to the reaction flask and treated with sodium hydroxide and vanillin in exactly the same manner as described in the last experiment. The work up and yields of products were identical.

Reaction of Vanillin with Alkali and One-fourth Mole Silver Oxide.—One-fourth mole of freshly prepared silver oxide (from 85.0 g. of silver nitrate) was covered with 1000 cc. of water and treated in succession with 160 g. (4 moles) of sodium hydroxide and 152 g. (1.0 mole) of vanillin with vigorous stirring. The reaction took place exactly as the one described directly above. When the reaction mixture began to cool, heat was applied and the mixture was boiled under reflux for one hour. After filtering and washing the silver precipitate with water, the filtrate was cooled and saturated with carbon dioxide. A yellow semisolid precipitate separated while the solution was still strongly alkaline. The mixture was extracted with ether, and the ether was dried with sodium sulfate and distilled under reduced pressure to give 34.2 g. (0.26 mole) of yellow solid which was recrystallized from either water or ligroin to white silky needles of 4,4′-dihydroxy-3,3′-dimethoxydiphenylmethane melting at 108–109°.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.20; H, 6.20; CH_3O, 23.85. Found: C, 68.99; H, 6.23; CH_3O, 23.69.

The aqueous carbonated layer was acidified with dilute sulfuric acid, filtered, and the precipitate was dried. Pure white vanillic acid, weighing 119.6 g. (0.71 mole) and melting at 209–210°, was obtained. Another 5.1 g. (0.03 mole) of vanillic acid was obtained on extraction of the filtrate with ether and recrystallization of the extract from water.

4,4′-Dibenzoxy-3,3′-dimethoxydiphenylmethane.—4,4′-Dihydroxy-3,3′-dimethoxydiphenylmethane was shaken with an excess of benzoyl chloride in *N* sodium hydroxide solution, and the precipitated benzoate was filtered. Recrystallization from methanol or ethanol yielded white translucent platelets melting at 133–134°.

Anal. Calcd. for $C_{29}H_{24}O_6$: C, 74.3; H, 5.17. Found: C, 73.92; H, 5.29.

3,4,3′,4′-Tetramethoxydiphenylmethane.[16]—Attempts to methylate 4,4′-dihydroxy-3,3′-dimethoxydiphenylmethane with diazomethane resulted in recovery of only the starting material. A solution of 4,4′-dihydroxy-3,3′-dimethoxydiphenylmethane in 5% sodium hydroxide was treated with an excess of dimethyl sulfate. The mixture was vigorously shaken while warming on the steam-bath. After several minutes oily drops settled out and, on cooling, these solidified. The mixture was extracted with ether, and the ether was dried and distilled. The residue, recrystallized from petroleum ether, was obtained as white leaflets melting at 70–71°.

Anal. Calcd. for $C_{17}H_{20}O_4$: CH_3O, 43.07. Found: CH_3O, 42.84.

Reaction of Vanillyl Alcohol with Alkali and One Mole Silver Oxide.[20]—A vigorously stirred suspension of 0.02 mole of freshly prepared silver oxide in 50 ml. of water was treated with 4.0 g. (0.10 mole) of sodium hydroxide, warmed to 75°, and then treated with 3.08 g. (0.02 mole) of powdered vanillyl alcohol at one time. The silver oxide was reduced immediately and fine gas bubbles were evolved. After several minutes the mixture was filtered and the reduced fluffy silver was thoroughly washed with water. The combined filtrate and washings were acidified with sulfur dioxide and extracted with ether. The ether was dried and distilled to yield 3.12 g. (93%) of vanillic acid as white crystals melting at 207–208°. Recrystallization from water gave pure vanillic acid melting at 210–211° which did not depress a mixed melting point with authentic vanillic acid.

The sulfur dioxide saturated aqueous layer was further acidified with sulfuric acid, aspirated, and extracted with ether. No vanillin could be found in the trace of residue obtained.

Reaction of Vanillyl Alcohol with Alkali.—A mixture of 15.4 g. (0.1 mole) of vanillyl alcohol, 40 g. (1.0 mole) of sodium hydroxide, and 400 cc. of water was heated to boiling with stirring and allowed to cool. The clear solution was saturated with carbon dioxide. While strongly alkaline, a light semi-solid precipitate separated. The mixture was extracted with ether, and the ether was dried and distilled. The residue, weighing 12.9 g., was recrystallized from ligroin to give white needles melting at 108–109°. The melting point of a mixture with authentic 4,4′-dihydroxy-3,3′-dimethoxydiphenylmethane was not depressed.

Addition of 0.1 mole of vanillic acid to the above mixture did not change the course of the reaction. All of the vanillic acid was recovered from the carbonated aqueous solution.

Reaction of Vanillin with Alkali and Cupric Oxide Containing a Trace of Silver Oxide.—A mixture of 50 g. (0.2 mole) of hydrated copper sulfate, 0.5 g. (1% of the copper sulfate) of silver nitrate, and 500 cc. of water was heated to boiling and treated with a boiling solution of 17 g. (0.42 mole) of sodium hydroxide in 500 cc. of water. The black precipitate was filtered and washed with hot water. The wet oxide was transferred to a 1-liter flask, covered with 500 cc. of water, and treated with 8.2 g. (0.205 mole) of sodium hydroxide and 15.2 g. (0.1 mole) of vanillin. The mixture was boiled under reflux for two hours and allowed to cool. The brown-black precipitate was filtered and washed with water. The filtrate and washings were acidified with sulfur dioxide, cooled, and extracted with ether. The ether was dried and distilled leaving 0.45 g. of vanillic acid melting at 207–209°. The sulfur dioxide-saturated solution was further acidified with sulfuric acid, aspirated to remove all sulfur dioxide, and extracted with ether. The ether upon drying and distilling yielded 14.41 g. of vanillin melting at 76–78°. The vanillic acid yield corresponded to 91% based on the silver nitrate used, and the vanillin recovery amounted to 97.9%.

Acknowledgment.—The author is indebted to the Analytical Department of The Institute of Paper Chemistry for the analyses reported in this paper.

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(20) Inserted Dec. 26, 1945—*Editor.*

Summary

Vanillin has been substantially quantitatively oxidized to vanillic acid by means of alkali and one-half mole of silver oxide. A Cannizzaro reaction mechanism for this reaction has been proposed. The alcohol product of the Cannizzaro reaction of vanillin has been identified as 4,4'-dihydroxy-3,3'-dimethoxydiphenylmethane.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

An Analysis of the Streaming Potential Method of Measuring the Potential at the Interface between Solids and Liquids

BY LLOYD A. WOOD

A previous publication[1] describes in detail an improved method of measuring the streaming potential produced by flow of water solutions through a capillary, and measurements with capillaries of vitreous silica and dilute solutions of potassium chloride are reported. It is the purpose here to inquire into the physical significance of the streaming potential measurements and to establish the criteria and assumptions necessary to convert them into reliable zeta-potentials.

The Helmholtz Concept of the Electric Double Layer, and Subsequent Modifications.—Helmholtz,[2] who originally formulated the concept of the electric double layer and the equations of electrokinetics, assumed that there is an immobile layer of electric charges on the solid at a solid–liquid interface, and another sharply defined mobile layer of charges of opposite polarity parallel to the interface a short distance away in the interior of the liquid. Movement of one phase relative to the other results in electrokinetic effects such as the streaming potential. It is now realized that the solution layer must be diffuse, and the revision of Helmholtz's reasoning to conform to a charge distribution according to an exponential law was first carried out by Gouy.[3] Smoluchowski[4] later generalized the electrokinetic equations and showed them to be applicable to any distribution of charges in the solution.

It appears, however, that some of the clarity of understanding of the electrokinetic effects demonstrated by Helmholtz has been lost in subsequent discussions. The first property of the double layer discussed by him is the moment, which he defined as the quantity σd (where σ is the charge density, or number of charges per unit area, on the solid surface, and d is the distance between the two layers), and this is equal to the potential difference $(\psi_1 - \psi_2)$, the zeta-potential, between the two layers divided by the constant 4π. (He did not take into account the dielectric constant, D, of the medium between the layers, and therefore the relation should be $\sigma d = (\psi_1 - \psi_2)D/4\pi$.) While it is true that he referred almost exclusively to the potential in his arguments in developing the theory, it is noteworthy that he frequently referred to the moment, particularly when discussing experimental measurements, in such a way as to show that to him the moment and potential were synonymous.[5] This was dimensionally correct because at that time it was conventional to express electrical quantities in three fundamental dimensions: mass, length and time. The charge density has the dimensions $\mathrm{M}^{1/2}\mathrm{L}^{-1/2}\mathrm{T}^{-1}$ which when multiplied by the length d gives the dimensions of potential $\mathrm{M}^{1/2}\mathrm{L}^{1/2}\mathrm{T}^{-1}$.

Subsequent writers on electrokinetics have generally ignored the moment and focussed their attention exclusively upon the zeta-potential, probably because potential theory has been well developed, and the potential seems more familiar and is generally easier to handle mathematically. Furthermore, since Helmholtz's time it has become conventional in electrostatics to assign four dimensions to fundamental quantities: if the dielectric constant is taken as the fourth dimension, then the potential has the dimensions $\mathrm{D}^{-1/2}\mathrm{M}^{1/2}\mathrm{L}^{1/2}\mathrm{T}^{-1}$ and the moment of the double layer the dimensions $\mathrm{D}^{1/2}\mathrm{M}^{1/2}\mathrm{L}^{1/2}\mathrm{T}^{-1}$. With this convention the moment and potential are not the same kind of quality. Guggenheim,[6] in a study of this question, expressed concern over the apparent neglect of fundamental units in the electrokinetic equations, but this is unwarranted and the result of an inconsistency in his own conventions. He chose four fundamental units: length, time, energy and charge, in which to express electrical units, and then defined the dielectric constant as a dimensionless measure-ratio. If the dielectric constant is dimensionless, then the dimension of charge can be expressed in terms of the other dimensions by means of the fundamental equation of electrostatics. The force f on a charge q exerted by another charge q' at a distance r in a medium of dielectric constant D is given by: $f = qq'/Dr^2$. Thus if D is dimensionless, the charge has the

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(1) Grinnell Jones and L. A. Wood, *J. Chem. Phys.*, **13**, 106 (1945).

(2) H. Helmholtz, *Wied. Ann.*, **7**, 337 (1879).

(3) L. Gouy, *J. phys.*, **9**, 457 (1910).

(4) M. Smoluchowski in Graetz, "Handbuch der Electrizität und des Magnetismus," Vol. II, Verlag Johann Barth, Leipzig, 1921, p. 374.

(5) For example, see ref. 2, pp. 358–359, 370, 382.

(6) E. A. Guggenheim, *Trans. Faraday Soc.*, **36**, 141 (1940).